10102-2

Gasoline Sulfur Reduction in Fluid Catalytic Cracking

5

Field of the Invention

This invention relates to the reduction of sulfur in gasolines and other petroleum products produced by the catalytic cracking process. The invention provides a catalytic

10   composition for reducing product sulfur and a process for reducing the product sulfur using this composition.

Cross Reference to Related Applications

15   This application is a continuation-in-part of prior Application Serial No. 09/221,540, filed 28 December 1998. It is also related to Application Serial No. 09/144,607, filed 31 August 1998.

Application Serial No. 09/ 221,539, filed 28 December 1998 (Mobil IP Case No. 10101-1,

20   PL 98-75) and its continuation-in-part, Serial No. 09/   , filed concurrently, (Mobil Case 10101-2) describes catalyst compositions for the reduction of sulfur in gasolines based on large pore zeolites, especially zeolite USY which contain vanadium and rarte earth cations.

25   **Background of the Invention**

Catalytic cracking is a petroleum refining process which is applied commercially on a very large scale, especially in the United States where the majority of the refinery gasoline blending pool is produced by catalytic cracking, with almost all of this coming

30   from the fluid catalytic cracking (FCC) process. In the catalytic cracking process heavy hydrocarbon fractions are converted into lighter products by reactions taking place at elevated temperature in the presence of a catalyst, with the majority of the conversion or cracking occurring in the vapor phase. The feedstock is so converted into gasoline,

distillate and other liquid cracking products as well as lighter gaseous cracking products of four or less carbon atoms per molecule. The gas partly consists of olefins and partly of saturated hydrocarbons.

5   During the cracking reactions some heavy material, known as coke, is deposited onto the catalyst. This reduces its catalytic activity and regeneration is desired. After removal of occluded hydrocarbons from the spent cracking catalyst, regeneration is accomplished by burning off the coke and then the catalyst activity is restored. The three characteristic steps of the catalytic cracking can be therefore be distinguished: a

10   cracking step in which the hydrocarbons are converted into lighter products, a stripping step to remove hydrocarbons adsorbed on the catalyst and a regeneration step to burn off coke from the catalyst. The regenerated catalyst is then reused in the cracking step.

Catalytic cracking feedstocks normally contain sulfur in the form of organic sulfur

15   compounds such as mercaptans, sulfides and thiophenes. The products of the cracking process correspondingly tend to contain sulfur impurities even though about half of the sulfur is converted to hydrogen sulfide during the cracking process, mainly by catalytic decomposition of non-thiophenic sulfur compounds. The distribution of sulfur in the cracking products is dependent on a number of factors including feed, catalyst type,

20   additives present, conversion and other operating conditions but, in any event a certain proportion of the sulfur tends to enter the light or heavy gasoline fractions and passes over into the product pool. With increasing environmental regulation being applied to petroleum products, for example in the Reformulated Gasoline (RFG) regulations, the sulfur content of the products has generally been decreased in response to concerns

25   about the emissions of sulfur oxides and other sulfur compounds into the air following combustion processes.

The environmental concerns have focussed extensively on the sulfur content of motor gasoline in view of its pre-eminent position as a vehicle fuel for passenger cars in the

30   United States. These concerns have, however, also extended to the higher boiling distillate fractions including the light cycle oil (LCO) and fuel oil fractions (light fuel oil, LFO, and heavy fuel oil, HFO) obtained from the catalytic cracking process. With these products, hydrodesulfurization has long been used to reduce the levels of sulfur in the

2

product fractions and, in general this has proved effective. The higher boiling fractions are not, however, as amenable to desulfurization as the lower boiling fractions because of the increasingly refractory nature of the sulfur compounds, especially the substituted benzothiophenes with increasing boiling point. In the LCO hydrodesulfurization process,

5   methyl and/or alkyl substitution of benzothiophene and dibenzothiophene makes desulfurization reactivity of the organic sulfurs decline substantially and they become "hard sulfur" or "refractory sulfur". An example of LCO sulfur GC is shown in Figure 1 with sulfur GC speciation. A review by Girgis and Gates, *Ind. Eng. Chem.*, *30*, 1991, 2021-2058. reported that substitution of a methyl group into the 4- position or into the 4-

10   and 6- positions decreases the desulfurization activity by an order of magnitude. Houalla et al. reported activity debits of 1-10 orders of magnitude, M. Houalla et al., *Journal of Catalysis*, *61*, 1980, 523-527. Lamure-Meille et al. suggested that steric hindrance of the alkyl group causes the low reactivity of methyl substituted dibenzothiophenes Lamure-Meille et al., *Applied Catalysis A*: General *131*, 1995, 143-157. Given the utilization of

15   the higher boiling catalytic cracking products as feeds for hydrodesulfurization processes, the incentive to reduce the incidence of the more refractory organic sulfur compounds in these cracking fractions becomes apparent.

One approach has been to remove the sulfur from the FCC feed by hydrotreating before

20   cracking is initiated. While highly effective, this approach tends to be expensive in terms of the capital cost of the equipment as well as operationally since hydrogen consumption is high. Another approach has been to remove the sulfur from the cracked products by hydrotreating. Again, while effective, this solution has the drawback that valuable product octane may be lost when the high octane olefins are saturated.

25

From the economic point of view, it would be desirable to achieve sulfur removal in the cracking process itself since this would effectively desulfurize the major component of the gasoline blending pool without additional treatment. Various catalytic materials have been developed for the removal of sulfur during the FCC process cycle but, so far, most

30   developments have centered on the removal of sulfur from the regenerator stack gases. An early approach developed by Chevron used alumina compounds as additives to the inventory of cracking catalyst to adsorb sulfur oxides in the FCC regenerator; the adsorbed sulfur compounds which entered the process in the feed were released as

3

hydrogen sulfide during the cracking portion of the cycle and passed to the product recovery section of the unit where they were removed. See Krishna et al, *Additives Improve FCC Process*, Hydrocarbon Processing, November 1991, pages 59-66. The sulfur is removed from the stack gases from the regenerator but product sulfur levels are not greatly affected, if at all.

An alternative technology for the removal of sulfur oxides from regenerator removal is based on the use of magnesium-aluminum spinels as additives to the circulating catalyst inventory in the FCCU. Under the designation DESOX™ used for the additives in this process, the technology has achieved a notable commercial success. Exemplary patents on this type of sulfur removal additive include U.S. 4,963,520; 4,957,892; 4,957,718; 4,790,982 and others. Again, however, product sulfur levels are not greatly reduced.

A catalyst additive for the reduction of sulfur levels in the liquid cracking products is proposed by Wormsbecher and Kim in U.S. Patents 5,376,608 and 5,525,210, using a cracking catalyst additive of an alumina-supported Lewis acid for the production of reduced-sulfur gasoline but this system has not achieved significant commercial success. The need for an effective additive for reducing the sulfur content of liquid catalytic cracking products has therefore persisted.

In Application Serial No. 09/144,607, filed 31 August 1998, we have described catalytic materials for use in the catalytic cracking process which are capable of reducing the sulfur content of the liquid products of the cracking process. These sulfur reduction catalysts comprise, in addition to a porous molecular sieve component, a metal in an oxidation state above zero within the interior of the pore structure of the sieve. The molecular sieve is in most cases a zeolite and it may be a zeolite having characteristics consistent with the large pore zeolites such as zeolite beta or zeolite USY or with the intermediate pore size zeolites such as ZSM-5. Non-zeolitic molecular sieves such as MeAPO-5, MeAPSO-5, as well as the mesoporous crystalline materials such as MCM-41 may be used as the sieve component of the catalyst. Metals such as vanadium, zinc, iron, cobalt, and gallium were found to be effective for the reduction of sulfur in the gasoline, with vanadium being the preferred metal. When used as a separate particle

4

additive catalyst, these materials are used in combination with the active catalytic cracking catalyst (normally a faujasite such as zeolite Y, especially as zeolite USY) to process hydrocarbon feedstocks in the fluid catalytic cracking (FCC) unit to produce low-sulfur. Since the sieve component of the sulfur reduction catalyst may itself be an active cracking catalyst, for instance, zeolite USY, it is also possible to use the sulfur reduction catalyst in the form of an integrated cracking/sulfur reduction catalyst system, for example, comprising USY as the active cracking component and the sieve component of the sulfur reduction system together with added matrix material such as silica, clay and the metal, e.g. vanadium, which provides the sulfur reduction functionality.

Another consideration in the manufacture of FCC catalysts has been catalyst stability, especially hydrothermal stability since cracking catalysts are exposed during use to repeated cycles of reduction (in the cracking step) followed by stripping with steam and then by oxidative regeneration which produces large amounts of steam from the combustion of the coke, a carbon-rich hydrocarbon, which is deposited on the catalyst particles during the cracking portion of the cycle. Early in the development of zeolitic cracking catalysts it was found that a low sodium content was required not only for optimum cracking activity but also for stability and that the rare earths such as cerium and lanthanum conferred greater hydrothermal stability. See, for example, *Fluid Catalytic Cracking with Zeolite Catalysts*, Venuto et al., Marcel Dekker, New York, 1979, ISBN 0-8247-6870-1.

Summary of the Invention

We have now developed catalytic materials for use in the catalytic cracking process which are capable of improving the reduction in the sulfur content of the liquid products of the cracking process including, in particular, the gasoline and middle distillate cracking fractions. The present sulfur reduction catalyst are similar to the ones described in Application No. 09/144,607 in that a metal component in an oxidation state above zero is present in the pore structure of a molecular sieve component of the catalyst composition, with preference again being given to vanadium. In the present case, however, the composition also comprises cerium. We have found that the presence of the cerium component not only enhances the stability of the catalyst, as compared to the catalysts

5

which contain only vanadium or another metal component (other than rare earth) but that it also increases the sulfur reduction activity. This is surprising since cerium in itself has no sulfur reduction activity.

5   The present sulfur reduction catalysts may be used in the form of an additive catalyst in combination with the active cracking catalyst in the cracking unit, that is, in combination with the conventional major component of the circulating cracking catalyst inventory which is usually a matrixed, zeolite containing catalyst based on a faujasite zeolite, usually zeolite Y. Alternatively, they may be used in the form of an integrated

10   cracking/product sulfur reduction catalyst system.

According to the present invention, the sulfur removal catalyst composition comprises a porous molecular sieve which contains (i) a metal in an oxidation state above zero within the interior of the pore structure of the sieve and (ii) a cerium component. The

15   molecular sieve is in most cases a zeolite and it may be a zeolite having characteristics consistent with the large pore zeolites such as zeolite beta or zeolite USY or with the intermediate pore size zeolites such as ZSM-5. Non-zeolitic molecular sieves such as MeAPO-5, MeAPSO-5, as well as the mesoporous crystalline materials such as MCM-41 may be used as the sieve component of the catalyst. Metals such as vanadium, zinc,

20   iron, cobalt, and gallium are effective. If the selected sieve material has sufficient cracking activity, it may be used as the active catalytic cracking catalyst component (normally a faujasite such as zeolite Y) or, alternatively, it may be used in addition to the active cracking component, whether or not it has any cracking activity of itself. The present compositions are useful to process hydrocarbon feedstocks in fluid catalytic

25   cracking (FCC) units to produce low-sulfur gasoline and other liquid products, for example, light cycle oil that can be used as a low sulfur diesel blend component or as heating oil.

The present compositions are useful to process hydrocarbon feedstocks in fluid catalytic

30   cracking (FCC) units to produce low-sulfur gasoline and other liquid products, for example, light cycle oil that can be used as a low sulfur diesel blend component or as heating oil. Besides achieving a very significant reduction in the sulfur content of the cracked gasoline fraction, the present sulfur reduction catalyst materials enable the

6

sulfur levels of light cycle oil and fuel oil products (light fuel oil, heavy fuel oil) to be reduced. The sulfur reduction in LCO occurs with the predominantly substituted-benzothiophenes and substituted-dibenzothiophenes; the removal of these more refractory species will improve the efficiency of sulfur reduction in subsequent LCO hydrodesulfurization process. The reduction in HFO sulfur may allow upgrading of coker products from the oil to premium coke.

While the mechanism by which the metal-containing zeolite catalyst compositions remove the sulfur components normally present in cracked hydrocarbon products is not precisely understood, it does involve the conversion of organic sulfur compounds in the feed to inorganic sulfur so that the process is a true catalytic process. In this process, it is believed that a zeolite or other molecular sieve provides shape selectivity with varying pore size, and the metal sites in zeolite provide adsorption sites for the sulfur species.

Drawings

The accompanying drawings are graphs showing the performance of the sulfur reduction catalysts as described below.

Detailed Description

FCC Process

The present sulfur removal catalysts are used as a catalytic component of the circulating inventory of catalyst in the catalytic cracking process, which these days is almost invariably the fluid catalytic cracking (FCC) process. For convenience, the invention will be described with reference to the FCC process although the present additives could be used in the older moving bed type (TCC) cracking process with appropriate adjustments in particle size to suit the requirements of the process. Apart from the addition of the present additive to the catalyst inventory and some possible changes in the product recovery section, discussed below, the manner of operating the process will remain unchanged. Thus, conventional FCC catalysts may be used, for example, zeolite based catalysts with a faujasite cracking component as described in the seminal review by

7

Venuto and Habib, *Fluid Catalytic Cracking with Zeolite Catalysts*, Marcel Dekker, New York 1979, ISBN 0-8247-6870-1 as well as in numerous other sources such as Sadeghbeigi, *Fluid Catalytic Cracking Handbook*, Gulf Publ. Co. Houston, 1995, ISBN 0-88415-290-1.

Somewhat briefly, the fluid catalytic cracking process in which the heavy hydrocarbon feed containing the organosulfur compounds will be cracked to lighter products takes place by contact of the feed in a cyclic catalyst recirculation cracking process with a circulating fluidizable catalytic cracking catalyst inventory consisting of particles having a size ranging from about 20 to about 100 microns. The significant steps in the cyclic process are:

(i) the feed is catalytically cracked in a catalytic cracking zone, normally a riser cracking zone, operating at catalytic cracking conditions by contacting feed with a source of hot, regenerated cracking catalyst to produce an effluent comprising cracked products and spent catalyst containing coke and strippable hydrocarbons;

(ii) the effluent is discharged and separated, normally in one or more cyclones, into a vapor phase rich in cracked products and a solids rich phase comprising the spent catalyst;

(iii) the vapor phase is removed as product and fractionated in the FCC main column and its associated side columns to form liquid cracking products including gasoline and cycle oil (which can be fractionated further into light cycle oil and heavy cycle oil),

(iv) the spent catalyst is stripped, usually with steam, to remove occluded hydrocarbons from the catalyst, after which the stripped catalyst is oxidatively regenerated to produce hot, regenerated catalyst which is then recycled to the cracking zone for cracking further quantities of feed.

The feed to the FCC process will typically be a high boiling feed of mineral oil origin, normally with an initial boiling point of at least 290°C (about 550°F) and in most cases above 315° C (about 600°F). Most refinery cut points for FCC feed will be at least 345°C (about 650°F). The end point will vary, depending on the exact character of the feed or on the operating characteristics of the refinery. Feeds may be either distillate, typically with an end point of 550°C (about 1020°F) or higher, for example, 590°C (about 1095°F)

or 620°C (about 1150°F) or, alternatively, resid (non-distillable) material may be included in the feed and may even comprise all or a major proportion of the feed. Distillable feeds include virgin feeds such as gas oils, e.g. heavy or light atmospheric gas oil, heavy or light vacuum gas oil as well as cracked feeds such as light coker gas oil, heavy coker

5   gas oil. Hydrotreated feeds may be used, for example, hydrotreated gas oils, especially hydrotreated heavy gas oil but since the present catalysts are able to effect a considerable reduction in sulfur, it may be possible to dispense with initial hydrotreatment where its objective is to reduce sulfur although improvements in crackability will still be achieved.

10

In the present process, the sulfur content of the gasoline portion of the liquid cracking products, is effectively brought to lower and more acceptable levels by carrying out the catalytic cracking in the presence of the sulfur reduction catalyst.

15   *FCC Cracking Catalyst*

The present sulfur reduction catalyst compositions may be used in the form of a separate particle additive which is added to the main cracking catalyst in the FCCU or, alternatively, they may be used as components of the cracking catalyst to provide an

20   integrated cracking/sulfur reduction catalyst system. The cracking component of the catalyst which is conventionally present to effect the desired cracking reactions and the production of lower boiling cracking products, is normally based on a faujasite zeolite active cracking component, which is conventionally zeolite Y in one of its forms such as calcined rare-earth exchanged type Y zeolite (CREY), the preparation of which is

25   disclosed in U.S. Patent No. 3,402,996, ultrastable type Y zeolite (USY) as disclosed in U.S. Patent No. 3,293,192, as well as various partially exchanged type Y zeolites as disclosed in U.S. Patents Nos. 3,607,043 and 3,676,368. Cracking catalysts such as these are widely available in large quantities from various commercial suppliers. The active cracking component is routinely combined with a matrix material such as silica or

30   alumina as well as a clay in order to provide the desired mechanical characteristics (attrition resistance etc.) as well as activity control for the very active zeolite component or components. The particle size of the cracking catalyst is typically in the range of 10 to 100 microns for effective fluidization. If used as a separate particle additive, the sulfur

9

reduction catalyst (and any other additive) is normally selected to have a particle size and density comparable to that of the cracking catalyst so as to prevent component separation during the cracking cycle.

5   *Sulfur Reduction System - Sieve Component*

According to the present invention, the sulfur removal catalyst comprises a porous molecular sieve which contains a metal in an oxidation state above zero within the interior of the pore structure of the sieve.   The molecular sieve is in most cases a zeolite

10   and it may be a zeolite having characteristics consistent with the large pore zeolites such as zeolkite Y, preferably zeolite USY, or zeolite beta or with the intermediate pore size zeolites such as ZSM-5, with the former class being preferred.

The molecular sieve component of the present sulfur reduction catalysts may, as noted

15   above, be a zeolite or a non-zeolitic molecular sieve.   When used, zeolites may be selected from the large pore size zeolites or intermediate pore zeolites (see *Shape Selective Catalysis in Industrial Applications*, Chen et al, Marcel Dekker Inc., New York 1989, ISBN 0-8247-7856-1, for a discussion of zeolite classifications by pore size according to the basic scheme set out by Frilette et al in *J. Catalysis* 67, 218-222

20   (1981)). The small pore size zeolites such as zeolite A and erionite, besides having insufficient stability for use in the catalytic cracking process, will generally not be preferred because of their molecular size exclusion properties which will tend to exclude the   components of the cracking feed as well as many components of the cracked products. The pore size of the sieve does not, however, appear to be critical since, as

25   shown below, both medium and large pore size zeolites have been found to be effective, as have the mesoporous crystalline materials such as MCM-41.

Zeolites having properties consistent with the existence of a large pore (12 ring) structure which may be used to make the present sulfur reduction catalysts include zeolites Y in its

30   various forms such as Y, REY, CREY, USY, of which the last is preferred, as well as other zeolites such as zeolite L, zeolite beta, mordenite including de-aluminated mordenite, and zeolite ZSM-18. Generally, the large pore size zeolites are characterized by a pore structure with a ring opening of at least 0.7 nm and the medium or intermediate

10

pore size zeolites will have a pore opening smaller than 0.7 nm but larger than about 0.56 nm. Suitable medium pore size zeolites which may be used include the pentasil zeolites such as ZSM-5, ZSM-22, ZSM-23, ZSM-35, ZSM-50, ZSM-57, MCM-22, MCM-49, MCM-56 all of which are known materials. Zeolites may be used with framework metal elements other than aluminum, for example, boron, gallium, iron, chromium.

The use of zeolite USY is particularly desirable since this zeolite is typically used as the active cracking component of the cracking catalyst and it is therefore possible to use the sulfur reduction catalyst in the form of an integrated cracking/sulfur reduction catalyst system. The USY zeolite used for the cracking component may also, to advantage, be used as the sieve component for a separate particle additive catalyst as it will continue to contribute to the cracking activity of the overall catalyst present in the unit. Stability is correlated with low unit cell size with USY and, for optimum results, the UCS for the USY zeolite in the finished catalyst should be from 2.420 to 2.455 nm, preferably 2.420 to 2.445 nm, with the range of 2.435 to 2.440 nm being very suitable. After exposure to the repeated steaming of the FCC cycles, further reductions in UCS will take place to a final value which is normally within the range of 2.420 to 2.430 nm

In addition to the zeolites, other molecular sieves may be used although they may not be as favorable since it appears that some acidic activity (conventionally measured by the alpha value) is required for optimum performance. Experimental data indicate that alpha values in excess of about 10 (sieve without metal content) are suitable for adequate desulfurization activity, with alpha values in the range of 0.2 to 2,000 being normally suitable[1]. Alpha values from 0.2 to 300 represent the normal range of acidic activity for these materials when used as additives.

Exemplary non-zeolitic sieve materials which may provide suitable support components for the metal component of the present sulfur reduction catalysts include silicates (such as the metallosilicates and titanosilicates) of varying silica-alumina ratios,

---

[1]   The alpha test is a convenient method of measuring the overall acidity, inclusive of both its internal and external acidity, of a solid material such as a molecular sieve. The test is described in U.S. Pat. No. 3,354,078; in the Journal of Catalysis, Vol. 4, p. 527 (1965); Vol. 6, p. 278 (1966); and Vol. 61, p. 395 (1980). Alpha values reported in this specification are measured at a constant temperature of 538°C.

metalloaluminates (such as germaniumaluminates), metallophosphates, aluminophosphates such as the silico- and metalloaluminophosphates referred to as metal integrated aluminophosphates (MeAPO and ELAPO), metal integrated silicoaluminophosphates (MeAPSO and ELAPSO), silicoaluminophosphates (SAPO), gallogermanates and combinations of these. A discussion on the structural relationships of SAPO's, AIPO's, MeAPO's, and MeAPSO's may be found in a number of resources including *Stud. Surf. Catal.* 37 13 - 27 (1987). The AIPO's contain aluminum and phosphorus, whilst in the SAPO's some of the phosphorus and/or some of both phosphorus and aluminum is replaced by silicon. In the MeAPO's various metals are present, such as Li, B, Be, Mg, Ti, Mn, Fe, Co, An, Ga, Ge, and As, in addition to aluminum and phosphorus, whilst the MeAPSO's additionally contain silicon. The negative charge of the $Me_aAl_bP_cSi_dO_e$ lattice is compensated by cations, where Me is magnesium, manganese, cobalt, iron and/or zinc. Me_xAPSOs are described in U.S. Pat. No. 4,793,984. SAPO-type sieve materials are described in U.S. Pat. No. 4,440,871; MeAPO type catalysts are described in U.S. Pat. Nos. 4,544,143 and 4,567,029; ELAPO catalysts are described in U.S. Pat. No. 4,500,651, and ELAPSO catalysts are described in European Patent Application 159,624. Specific molecular sieves are described, for example, in the following patents: MgAPSO or MAPSO-U.S. Pat. No. 4,758,419. MnAPSO-U.S. Pat. No. 4,686,092; CoAPSO-U.S. Pat. No. 4,744,970;FeAPSO-U.S. Pat. No. 4,683,217 and ZnAPSO U.S. Pat. No. 4,935,216. Specific silicoaluminophosphates which may be used include SAPO-11, SAPO-17, SAPO-34, SAPO-37; other specific sieve materials include MeAPO-5, MeAPSO-5.

Another class of crystalline support materials which may be used is the group of mesoporous crystalline materials exemplified by the MCM-41 and MCM-48 materials. These mesoporous crystalline materials are described in U.S. Patents Nos. 5,098,684; 5,102,643; and 5,198,203. MCM-41, which is described in U.S. 5,098,684, is characterized by a microstructure with a uniform, hexagonal arrangement of pores with diameters of at least about 1.3 nm: after calcination it exhibits an X-ray diffraction pattern with at least one d-spacing greater than about 1.8 nm and a hexagonal electron diffraction pattern that can be indexed with a d100 value greater than about 1.8 nm which corresponds to the d-spacing of the peak in the X-ray diffraction pattern. The preferred catalytic form of this material is the aluminosilicate although other

12

metallosilicates may also be utilized. MCM-48 has a cubic structure and may be made by a similar preparative procedure.

Metal Components

Two metal components are incorporated into the molecular sieve support material to make up the present catalytic compositions. One component is cerium which is thought to be present in the form of cations within the pore structure of the sieve. The other metal component can be regarded as the primary sulfur reduction component although the manner in which it effects sulfur reduction is not clear, as discussed in Application Serial No. 09/144,607, to which reference is made for a description of sulfur reduction catalyst compositions containing vanadium and other metal components effective for this purpose. For convenience this component of the composition will be referred to in this application as the primary sulfur reduction component. In order to be effective, this metal (or metals) should be present inside the pore structure of the sieve component. Metal-containing zeolites and other molecular sieves can be prepared by (1) post-addition of metals to the sieve or to a catalyst containing the sieve(s), (2) synthesis of the sieve(s) containing metal atoms in the framework structure, and by (3) synthesis of the sieve(s) with trapped, bulky metal ions in the zeolite pores. Following addition of the metal component, washing to remove unbound ionic species and drying and calcination should be performed. These techniques are all known in themselves. Post-addition of the metal ions is preferred for simplicity and economy, permitting available sieve materials to be converted to use for the present additives. A wide variety of post-addition methods of metals can be used to produce a catalyst of our invention, for example, aqueous exchange of metal ions, solid-state exchange using metal halide salt(s), impregnation with a metal salt solution, and vapor deposition of metals. In each case, however, it is important to carry out the metal(s) addition so that the metal component enters the pore structure of the sieve component.

It has been found that when the metal of the primary sulfur reduction component is present as exchanged cationic species in the pores of the sieve component, the hydrogen transfer activity of the metal component is reduced to the point that hydrogen transfer reactions taking place during the cracking process will normally maintained at

13

an acceptably low level with the preferred metal components. Thus, coke and light gas make during cracking increase slightly but they remain within tolerable limits. Since the unsaturated light ends can be used in any event as alkylation feed and in this way recycled to the gasoline pool, there is no significant loss of gasoline range hydrocarbons

5   incurred by the use of the present additives.

Because of the concern for excessive coke and hydrogen make during the cracking process, the metals for incorporation into the additives should not exhibit hydrogenation activity to a marked degree. For this reason, the noble metals such as platinum and

10   palladium which possess strong hydrogenation-dehydrogenation functionality are not desirable. Base metals and combinations of base metals with strong hydrogenation functionality such as nickel, molybdenum, nickel-tungsten, cobalt-molybdenum and nickel-molybdenum are not desirable for the same reason. The preferred base metals are the metals of Period 3, Groups 5, 8, 9, 12, (IUPAC classification, previously Groups

15   2B, 5B and 8B) of the Periodic Table. Vanadium, zinc, iron, cobalt, and gallium are effective with vanadium being the preferred metal component. It is surprising that vanadium can be used in this way in an FCC catalyst composition since vanadium is normally thought to have a very serious effect on zeolite cracking catalysts and much effort has been expended in developing vanadium suppressers. See, for example,

20   Wormsbecher et al, *Vanadium Poisoning of Cracking Catalysts: Mechanism of Poisoning and Design of Vanadium Tolerant Catalyst System*, J. Catalysis 100, 130-137 (1986). It is believed that the location of the vanadium inside the pore structure of the sieve immobilizes the vanadium and prevents it from becoming vanadic acid species which can combine deleteriously with the sieve component; in any event, the present zeolite-

25   based sulfur reduction catalysts containing vanadium as the metal component have undergone repeated cycling between reductive and oxidative/steaming conditions representative of the FCC cycle while retaining the characteristic zeolite structure, indicating a different environment for the metal.

30   Vanadium is particularly suitable for gasoline sulfur reduction when supported on zeolite USY. The yield structure of the V/USY sulfur reduction catalyst is particularly interesting. While other zeolites, after metals addition, demonstrate gasoline sulfur reduction, they tend to convert gasoline to C_3 and C_4 gas. Even though much of the converted $C_3=$ and

14

C_4= can be alkylated and re-blended back to the gasoline pool, the high C_4- wet gas yield may be a concern since many refineries are limited by their wet gas compressor capacity. The metal-containing USY has similar yield structure to current FCC catalysts; this advantage would allow the V/USY zeolite content in a catalyst blend to be adjusted

5   to a target desulfurization level without limitation from FCC unit constraints. The vanadium on Y zeolite catalyst, with the zeolite represented by USY, is therefore a particularly favorable combination for gasoline sulfur reduction in FCC. The USY which has been found to give particularly good results is a USY with low unit cell size in the range from 2.420 to 2.450 nm, preferably 2.435 to 2.450 nm (following treatment) and a

10 correspondingly low alpha value. Combinations of base metals such as vanadium/zinc as the primary sulfur reduction component may also be favorable in terms of overall sulfur reduction.

     The amount of the primary sulfur reduction metal component in the sulfur reduction

15 catalyst is normally from 0.1 to 10 weight percent, typically 0.25 to 5 weight percent, (as metal, relative to weight of sieve component) but amounts outside this range, for example, up to 10 weight percent may still be found to give some sulfur removal effect. When the sieve is matrixed, the amount of the primary sulfur reduction metal component expressed relative to the total weight of the catalyst composition will, for practical

20 purposes of formulation, typically extend from 0.05 to 5, more typically from 0.1 to 3 weight percent of the entire catalyst.

     The second metal component of the sulfur reduction catalyst composition comprises cerium which is present within the pore structure of the molecular sieve and is thought to

25 be present in the form of cations exchanged onto the exchangeable sites present on the sieve component. The cerium component significantly not only improves the catalyst stability in the presence of vanadium (or other primary sulfur reduction metal component) but also enhances the sulfur reduction activity of the catalyst. For example, higher cracking activity can be achieved with a Ce/V/USY catalyst compared to a V/USY

30 catalyst, while comparable gasoline sulfur reduction is obtained. In Application Serial No. 09/   , filed concurrently with this application (Mobil IP Case 10101-2, PL 98-75, continuation-in-part of Serial No. 09/221539), we show that other rare earths are

effective for improving catalyst stability when vanadium is present and that combinations of rare earth with cerium are capable of improving sulfur reduction.

5   The amount of cerium is typically from 0.1 to 10 wt. percent of the catalyst composition, in most cases from 0.25 to 5 wt. percent. Relative to the weight of the sieve, the amount of the rare earth will normally be from about 0.2 to 20 weight percent and in most cases from 0.5 to 10 weight percent of the sieve, depending on the sieve:matrix ratio.

10   The rare earth component can suitably be incorporated into the molecular sieve component by exchange onto the sieve, either in the form of theunmatrixed crystal or of the matrixed catalyst. When the composition is being formulated with the preferred USY zeolite sieve, a very effective manner of incorporation is to add the rare earth ions to the USY sieve (typically 2.445 – 2.465 nm unit cell size) followed by additional steam calcination to lower the unit cell size of the USY to a value typically in the range of 2.420
15   to 2.450, preferably 2.430 to 2.445 nm., after which the primary metal component may be added if not already present. The USY should have a low alkali metal (mainly sodium) content for stability as well as for satisfactory cracking activity; this will normally be secured by the ammonium exchange made during the ultrastabilization process to a desirable low sodium level of not more than 1 weight percent, preferably not more than
20   0.5 weight percent, on the sieve.

     The metal components are incorporated into the catalyst composition in a way which ensures that they enter the interior pore structure of the sieve. The metals may be incorporated directly into the crystal or into the matrixed catalyst. When using the
25   preferred USY zeolite as the sieve component, this can suitably be done as described above, by recalcining a USY cracking catalyst containing the cerium component to ensure low unit cell size and then incorporating the metal, e.g. vanadium, by ion exchange or by impregnation under conditions which permit cation exchange to take place so that the metal ion is immobilized in the pore structure of the zeolite.
30   Alternatively, the primary sulfur reduction component and the cerium component can be incorporated into the sieve component, e.g. USY zeolite or ZSM-5 crystal, after any necessary calcination to remove organics from the synthesis after which the metal-containing component can be formulated into the finished catalyst composition by the

addition of the cracking and matrix components and the formulation spray dried to form the final catalyst.

When the catalyst is being formulated as an integrated catalyst system, it is preferred to use the active cracking component of the catalyst as the sieve component of the sulfur reduction system, preferably zeolite USY, both for simplicity of manufacture but also for retention of controlled cracking properties. It is, however, possible to incorporate another active cracking sieve material such as zeolite ZSM-5 into an integrated catalyst system and such systems may be useful when the properties of the second active sieve material are desired, for instance, the properties of ZSM-5. The impregnation/exchange process should in both cases be carried out with a controlled amount of metal so that the requisite number of sites are left on the sieve to catalyze the cracking reactions which may be desired from the active cracking component or any secondary cracking components which are present, e.g. ZSM-5.

Use of Sulfur Reduction Catalyst Composition

Normally the most convenient manner to use the sulfur reduction catalyst will be as a separate particle additive to the catalyst inventory. In its preferred form, with zeolite USY as the sieve component, the addition of the catalyst additive to the total catalyst inventory of the unit will not result in significant reduction in overall cracking because of the cracking activity of the USY zeolite. The same is true when another active cracking material is used as the sieve component. When used in this way, the composition may be used in the form of the pure sieve crystal, pelleted (without matrix but with added metal components) to the correct size for FCC use. Normally, however, the metal-containing sieve will be matrixed in order to achieve adequate particle attrition resistance and to maintain satisfactory fluidization. Conventional cracking catalyst matrix materials such as alumina or silica-alumina, usually with added clay, will be suitable for this purpose. The amount of matrix relative to the sieve will normally be from 20:80 to 80:20 by weight. Conventional matrixing techniques may be used.

Use as a separate particle catalyst additive permits the ratio of sulfur reduction and cracking catalyst components to be optimized according to the amount of sulfur in the

17

feed and the desired degree of desulfurization; when used in this manner, it is typically used in an amount from 1 to 50 weight percent of the entire catalyst inventory in the FCCU; in most cases the amount will be from 5 to 25 weight percent, e.g. 5 to 15 weight percent. About 10 percent represents a norm for most practical purposes. The additive

5   may be added in the conventional manner, with make-up catalyst to the regenerator or by any other convenient method. The additive remains active for sulfur removal for extended periods of time although very high sulfur feeds may result in loss of sulfur removal activity in shorter times.

10   The alternative to the use of the separate particle additive is to use the sulfur reduction catalyst incorporated into the cracking catalyst to form an integrated FCC cracking/gasoline sulfur reduction catalyst. If the sulfur reduction metal components are used in combination with a sieve other than the active cracking component, for example, on ZSM-5 or zeolite beta, when the main active cracking component is USY, the amount

15   of the sulfur reduction components (sieve plus metals) will typically be up to 25 weight percent of the entire catalyst or less, corresponding to the amounts in which it may be used as a separate particle additive, as described above.

Other catalytically active components may be present in the circulating inventory of

20   catalytic material in addition to the cracking catalyst and the sulfur removal additive. Examples of such other materials include the octane enhancing catalysts based on zeolite ZSM-5, CO combustion promoters based on a supported noble metal such as platinum, stack gas desulfurization additives such as DESOX™ (magnesium aluminum spinel), vanadium traps and bottom cracking additives, such as those described in

25   Krishna, Sadeghbeigi, *op cit.* and Scherzer, *Octane Enhancing Zeolitic FCC Catalysts*, Marcel Dekker, New York, 1990, ISBN 0-8247-8399-9. These other components may be used in their conventional amounts.

The effect of the present additives is to reduce the sulfur content of the liquid cracking

30   products, especially the light and heavy gasoline fractions although reductions are also achieved in the higher boiling distillate products including the light cycle oil and light and heavy fuel oil fractions, making this more amenable to hydrodesulfurization techniques by removal of the more refractory sulfur compounds. The distillate fractions may then

18

then be hydrodesulfurized under less severe, more economical conditions to produce distillate products suitable for use as a diesel or home heating oil blend component.

The cracking process itself will be carried out in the normal manner with the addition of the sulfur reduction catalyst, either in the form of an additive or as an integrated catalytic cracking/sulfur reduction catalyst (single particle catalyst). Cracking conditions will be conventional in nature.

The sulfur removed by the use of the catalyst is converted to inorganic form and released as hydrogen sulfide which can be recovered in the normal way in the product recovery section of the FCCU in the same way as the hydrogen sulfide conventionally released in the cracking process. The increased load of hydrogen sulfide may impose additional sour gas/water treatment requirements but with the significant reductions in gasoline sulfur achieved, these are not likely to be considered limiting.

Very significant reductions in cracked product sulfur can be achieved by the use of the present catalysts, in some cases up to about 50% relative to the base case using a conventional cracking catalyst, at constant conversion, using the preferred form of the catalyst described above. Gasoline sulfur reduction of 25 % is readily achievable with many of the additives according to the invention, as shown by the Examples below. For the middle distillate fractions including the LCO fraction, reductions of up to about 25 percent may also be achieved, as shown below in the Examples, coupled with a reduction in the level of refractory sulfur compounds including the alkyl substituted benzothiophenes and dibenzothiophenes. The extent of sulfur reduction may depend on the original organic sulfur content of the cracking feed, with the greatest reductions achieved with the higher sulfur feeds. The metals content of the equilibrium catalyst in the unit may also affect the degree of desulfurization achieved, with a low metals content, especially vanadium content, on the equilibrium catalyst favoring greater desulfurization. Desulfurization will be very effective with E-catalyst vanadium contents below 1,000 ppm although the present catalysts remain effective even at much higher vanadium contents. Sulfur reduction may be effective not only to improve product quality but also to increase product yield in cases where the refinery cracked gasoline end point has been limited by the sulfur content of the heavy gasoline fraction; by providing an

19

effective and economical way to reduce the sulfur content of the heavy gasoline fraction, the gasoline end point may be extended without the need to resort to expensive hydrotreating, with a consequent favorable effect on refinery economics. Removal of the various thiophene derivatives which are refractory to removal by hydrotreating under less
5   severe conditions is also desirable if subsequent hydrotreatment is contemplated.

Example 1
Preparation of Catalyst Series I
10
A V/USY catalyst, Catalyst A, was prepared using a commercial H-form USY (crystal) with a bulk silica-to-alumina ratio of 5.4 and 2.435 nm unit cell size. A fluid catalyst was prepared by spray drying aqueous slurry containing 40 wt% of the USY crystals, 25 wt% silica, 5 wt% alumina, and 30 wt% kaolin clay. The spray-dried catalyst was calcined at
15   540°C (1000°F) for 3 hours. The resulting H-form USY catalyst was impregnated with a vanadium oxalate solution to target 0.4 wt% V by incipient wetness impregnation. The impregnated V/USY catalyst was further air calcined at 540°C (1000°F) for 3 hours. The final catalyst contains 0.39% V.

20   A Ce+V/USY catalyst, Catalyst B, was prepared from the same, spray-dried H-form USY catalyst intermediate as Catalyst A. The H-form USY catalyst was impregnated with a solution of $Ce(NO_3)_3$ to target 1.5wt% Ce loading using an incipient wetness impregnation method. Resulting Ce/USY catalyst was air calcined at 540°C (1000°F) for 3 hours followed by steaming at 540°C (1000°F) for 3 hours. Then the catalyst was
25   impregnated with a vanadium oxalate solution to target 0.4 wt% V by incipient wetness impregnation. The impregnated Ce+V/USY catalyst was further air calcined at 540°C (1000°F) for 3 hours. The final catalyst contains 1.4% Ce and 0.43% V.

20

Table 1

Physical Properties of the V and Ce+V USY/ Silica-Alumina-Clay Catalysts

	V/USY Catalyst A	Ce+V/ USY Catalyst B
Calcined Cat.		
V loading, wt%	0.39	0.43
Ce loading, wt%	N.A.	1.4
Surface area, m^2g^{-1}	302	250
Alpha	130	12
UCS, nm	2.436	2.437

5 **Example 2**

Preparation of Catalyst Series 2

All samples in Catalyst Series 2 were prepared from a single source of spray dried material, consisting of 50% USY, 21% silica sol and 29% clay. The starting USY had a

10 bulk silica-to-alumina ratio of 5.4 and 2.435 nm unit cell size. The spray dried catalyst was slurried with a solution of $(NH_4)_2SO_4$ and NH_4OH at pH of 6 to remove Na^+, followed by washing with water and air calcination at 650°C (1200°F) for 2 hours.

A V/USY catalyst, Catalyst C, was prepared using the above H-form USY catalyst. The

15 H-form USY catalyst was impregnated with a vanadium oxalate solution to target 0.5 wt% V by incipient wetness impregnation. The impregnated V/USY catalyst was further air calcined at 650°C (1200°F) for 2 hours. The final catalyst contains 0.53% V.

A Ce+V/USY catalyst, Catalyst D, was prepared from the above H-form USY catalyst.

20 The H-form USY catalyst was exchanged with a solution of $CeCl_3$ to target 0.75 wt% Ce loading. Resulting Ce/USY catalyst was air calcined and impregnated with a vanadium oxalate solution to target 0.5 wt% V by incipient wetness impregnation. The impregnated Ce+V/USY catalyst was further air calcined. The final catalyst contains 0.72% Ce and 0.52% V.

25

A Ce+V/USY catalyst, Catalyst E, was prepared from the above H-form USY catalyst by an exchange with a solution of $CeCl_3$ to target 3 wt% Ce loading. Resulting Ce/USY catalyst was air calcined and impregnated with a vanadium oxalate solution to target 0.5

wt% V by incipient wetness impregnation. The impregnated Ce+V/USY catalyst was further air calcined. The final catalyst contains 1.5% Ce and 0.53% V.

A Ce+V/USY catalyst, Catalyst F, was prepared from the above H-form USY catalyst by an incipient wetness impregnation with a solution of $CeCl_3$ to target 1.5 wt%Ce loading. Resulting Ce/USY catalyst was air calcined and impregnated with a vanadium oxalate solution to target 0.5 wt% V by incipient wetness impregnation. The impregnated Ce+V/USY catalyst was further air calcined. The final catalyst contains 1.5% Ce and 0.53% V.

These catalysts were then steamed deactivated, to simulate catalyst deactivation in an FCC unit, in a fluidized bed steamer at 770°C (1420°F) for 20 hours using 50% steam and 50% gas. The gas stream was changed from air, N_2, propylene, and to N_2 for every ten minutes, then circled back air to simulate the coking/ regeneration cycle of a FCC unit (cyclic steaming). Two samples of deactivated catalysts were generated: the steam deactivation cycle was ended with air-burn (ending-oxidation) for one batch of catalysts, and the other ended with propylene (ending-reduction). The coke content of the "ending-reduction" catalyst is less than 0.05% C. The physical properties of the calcined and steam deactivated catalysts are summarized in Table 2.

Table 2
Physical Properties of V and Ce+V USY/ Silica Sol Catalysts

	V/USY Catalyst C	Ce+V/ USY Catalyst D	Ce+V/ USY Catalyst E	Ce+V/ USY Catalyst F
Calcined Cat.				
V loading, wt%	0.53	0.52	0.53	0.53
Ce loading, wt%	N.A.	0.72	1.5	1.5
Na, ppm	890	1190	1190	1260
Deactivated Cat. (CPS 770°C, 20 hrs)				
Surface area, m^2g^{-1}	237	216	208	204
Unit cell size, nm	2.425	2.423	2.425	2.425

Example 3

Preparation of Catalyst Series 3

All samples in Catalyst Series 3 were prepared from a single source of spray dried material, consisting of 40% USY, 30% colloidal silica sol, and 30% clay. The starting H-form USY had a bulk silica-to-alumina ratio of 5.4 and 2.435nm unit cell size. The spray-dried catalyst was air calcined at 540°C (1000°F) for 3 hours.

A Ce/USY catalyst, Catalyst G, was prepared using the above H-form USY catalyst. The H-form USY catalyst was impregnated with a solution of $Ce(NO_3)_3$ to target 1.5wt% Ce loading using an incipient wetness impregnation method. Resulting Ce/USY catalyst was air calcined at 540°C (1000°F) followed by steaming at 540°C (1000°F) for 3 hours.

A Ce+V/USY catalyst, Catalyst H, was prepared from Catalyst G. The Ce/USY catalyst was impregnated with a vanadium oxalate solution to target 0.5 wt% V by incipient wetness impregnation. The impregnated Ce+V/USY catalyst was dried and air calcined at 540°C (1000°F) for 3 hours. The final catalyst contains 1.4% Ce and 0.49% V.

A Ce+V/USY catalyst, Catalyst I, was prepared from Catalyst G by an exchange with a solution of VOSO4 at pH ~3 to target 0.5 wt% V loading. Resulting Ce+V/USY catalyst was dried and air calcined at 540°C (1000°F) for 3 hours. The final catalyst contains 0.9% Ce and 0.47% V. Physical properties of calcined catalysts are summarized in Table 3.

Table 3
Physical Properties of the Ce and Ce+V USY/ Silica-Clay Catalysts

	Ce/USY Catalyst G	Ce+V/ USY Catalyst H	Ce+V/ USY Catalyst I
Calcined Cat.			
V loading, wt%	N.A.	0.49	0.47
Ce loading, wt%	1.6	1.4	0.9
Na, ppm	-	-	940
Surface area, m^2g^{-1}	284	281	272
Alpha	-	10	14
Unit cell size, nm	2.435	2.436	2.436

5

Example 4

Preparation of Ce+V/USY/Silica-Sol Catalyst

10   A Ce+V/USY catalyst, Catalyst J, was prepared using a NaUSY zeolite with a silica-to-alumina ratio of 5.5 and a unit cell size of 2.454 nm. The USY was exchanged with NH_4^+ by an exchange with a solution of ammonium sulfate. The NH_4^+ exchanged USY was then exchanged with Ce^{3+} cations by exchange with a solution of cerium chloride containing a small amount of other rare earth ions (e.g., La^{3+}, Pr,Nd, Gd, etc.). The Ce-

15   exchanged USY was further washed, dried, and calcined in the presence of steam at 705°C (1300°F) for 2 hours. The steam calcination lowered the unit cell size of the USY and improved its stability in the presence of vanadium. A fluid catalyst was prepared by spray drying an aqueous slurry containing 50 wt% Ce/USY crystals in a silica sol/clay matrix. The matrix contained 22-wt% silica sol and 28-wt% kaolin clay. The spray-dried

20   catalyst was exchanged with NH_4^+ by an exchange with a solution of ammonium sulfate and was then dried and calcined at 540°C (1000°F) for 1 hour. Following calcination, the Ce/USY catalyst was impregnated with a vanadium sulfate solution. Physical properties of the calcined catalyst are summarized in Table 4.

24

Tabl 4

Physical Properties of Ce+V/USY/ Silica-Sol Catalysts

	Ce+V/ USY Catalyst J
Calcined Cat.	
V loading, wt%	0.44
RE_2O_3 loading, wt%	2.66
CeO_2 loading, wt%	2.42
Na_2O, wt%	0.20
Surface area, m^2g^{-1}	345
Unit cell size, nm	2.446

5

Example 5

Fluid Catalytic Cracking Evaluation of Series 1 Catalysts

10   The V and Ce+V USY catalysts from Example 1 were steam deactivated in a fluidized bed steamer at 770°C (1420°F) for 20 hours using 50% steam and 50% gas. The gas stream was changed from air, N_2, propylene, and to N_2 for every ten minutes, then circled back air to simulate coking/ regeneration cycle of a FCC unit (cyclic steaming). The steam deactivation cycle was ended with air-burn (ending-oxidation). Twenty-five weight percent of steamed additive catalysts were blended with an equilibrium catalyst from an

15   FCC unit. The equilibrium catalyst has very low metals level (120 ppm V and 60 ppm Ni).

The procedure used for evaluating catalytic cracking performance of the catalysts described in this application comprised testing the blended catalysts for gas oil cracking

20   activity and selectivity using an ASTM microactivity test (ASTM procedure D-3907), using a vacuum gas oil (VGO) feed or a severely cat feed hydrotreated (CFHT) feed. The properties of the feedstocks are shown in Table 5 below. A range of conversions was scanned by varying the catalyst-to-oil ratios and reactions were run at 527°C (980°F). Gasoline range product from each material balance was analyzed with a sulfur

25   GC (AED) to determine the gasoline S concentration. To reduce experimental errors in S concentration associated with fluctuations in distillation cut point of gasoline, S species ranging from thiophene to C_4-thiophenes in syncrude (excluding benzothiophene and higher boiling S species) were quantitated and the sum was defined as "cut-gasoline S."

25

Table 5
Properties of Cracking Feeds

Charge Stock Properties	VGO	CFHT Feed
API Gravity	26.6	23.6
Aniline Point, °C	83	164
CCR, wt%	0.23	0.09
Sulfur, wt%	1.05	0.071
Nitrogen, ppm	600	1200
Basic nitrogen, ppm	310	380
Ni, ppm	0.32	0.2
V, ppm	0.68	0.2
Fe, ppm	9.15	0.3
Cu, ppm	0.05	0
Na, ppm	2.93	1.2
Distillation, °C		
IBP,	181	172
50 wt%,	380	373
99.5 wt%,	610	547

Performances of the Series 1 catalysts using the VGO feed are summarized in Table 6, where the product selectivity was interpolated to a constant conversion, 70wt% conversion of feed to 220°C- (430°F-) material.

Table 6
Catalytic Cracking Performance of Series 1 Catalysts

	ECat Base Case	+ 25% V/USY cat (Catalyst A)	+25% Ce+V/USY cat (Catalyst B)
MAT Product Yields			
Conversion, wt%	70	70	70
Cat/Oil	3.3	3.8	3.7
H2 yield, wt%	0.03	+0.04	+0.13
C1 + C2 Gas, wt%	1.4	+0.1	+0.1
Total C3 Gas, wt%	5.4	+0.1	-0.1
C3= yield, wt%	4.5	+0.1	-0.1
Total C4 Gas, wt%	10.9	+0.2	-0.2
C4= yield, wt%	5.2	+0.4	+0.2
iC4 yield, wt%	4.8	-0.2	-0.4
C5+ Gasoline, wt%	48.9	-0.3	-0.3
LFO, wt%	24.6	+0.5	+0.3
HFO, wt%	4.7	-0.2	-0.1
Coke, wt%	2.7	+0	+0.5
Cut Gasoline S, PPM	529	378	235
% Reduction in Cut Gasoline S	Base	29	56

Table 6 compares the FCC performances of V/USY and Ce+V/USY/ Silica-Alumina-Clay catalysts each blended with an equilibrium FCC catalyst (ECat) after cyclic steam deactivation (ending oxidation). Compared to the ECat base case, the addition of V/USY and Ce+V/USY catalyst changes the overall product yield structure only slightly. Yield changes in C4- gas, gasoline, light cycle oil, and heavy fuel oil are all small. Moderate increases in hydrogen and coke yields were observed. While the product yield changes were small, the V/USY and Ce+V/USY catalysts changed the gasoline S concentration substantially. When 25 wt% of Catalyst A (10 wt% V/USY zeolite addition, reference catalyst) was blended with an equilibrium FCC catalyst, 29% reduction in gasoline sulfur concentration was achieved. In comparison, Ce+V/ USY catalyst (Catalyst B) gave 56% reduction in gasoline S. Addition of Ce to the V/USY catalyst reduced the gasoline S content by additional 27%, i.e., 93% improvement over the V/USY reference catalyst.

Both catalysts have comparable vanadium loadings (0.39% vs. 0.43% V). In light of the fact that Ce by itself does not have any gasoline sulfur reduction activity (see below in Example 7), these results are quite unexpected and clearly demonstrate the benefits of cerium addition.

Example 6

Fluid Catalytic Cracking Evaluation of Series 2 Catalysts after Cyclic Steaming

The performances of V and Ce+V catalysts from Example 2 are summarized in this example. The Series 2 catalysts were steam deactivated as described above by cyclic steaming (ending-reduction), then blended with an equilibrium catalyst from an FCC unit in a 25:75 weight ratio and tested using the VGO feed. The equilibrium catalyst has very low metals level (120 ppm V and 60 ppm Ni). The results are summarized in Table 7.

Table 7
Catalytic Cracking Performance of V vs. Ce+V/USY/ Silica-Sol Catalysts

	ECat Base Case	+ 25% V/USY cat (Cat C)	+ 25% Ce+V/USY (Cat E)	+ 25% Ce+V/USY (Cat F)
MAT Product Yields				
Conversion, wt%	65	65	65	65
Cat/Oil	3.0	3.4	3.2	3.3
H2 yield, wt%	0.03	+0.02	+0.02	+0.02
C1 + C2 Gas, wt%	1.1	+0	+0	+0.1
Total C3 Gas, wt%	4.4	-0.1	-0.1	+0
C3= yield, wt%	3.7	+0	-0.1	+0
Total C4 Gas, wt%	9.5	-0.1	-0.2	-0.1
C4= yield, wt%	4.8	+0.1	+0.1	+0.1
iC4 yield, wt%	4.1	-0.2	-0.3	-0.1
C5+ Gasoline, wt%	47.4	+0.1	+0.5	+0.1
LFO, wt%	29.7	-0.2	+0	-0.1
HFO, wt%	5.3	+0.2	+0	+0.1
Coke, wt%	2.3	+0.1	-0.1	+0
Cut Gasoline S, PPM	516	489	426	426
% Reduction in Cut Gasoline S	Base	5.2	17.4	17.4

Table 6 compares FCC performances of V/USY and Ce+V/USY/ Silica-Sol additive catalysts after cyclic steam deactivation (ending-reduction).

Compared to the ECat base case, addition of the V/USY and Ce+V/USY catalysts made very little changes in the overall product yield structure. The yields of hydrogen, C4- gas, gasoline, light cycle oil, heavy fuel oil and coke were changed by less than 0.2 wt% each. Additions of the V/USY and Ce+V/USY catalysts changed the gasoline S concentration to different extents. When 25 wt% of Catalyst C (V/USY - reference catalyst) was blended with the equilibrium FCC catalyst, 5.2% reduction in gasoline sulfur concentration was achieved. For comparison, Ce+V/ USY catalysts (Catalysts E and F) gave 17.4% reduction in gasoline S, respectively. Addition of Ce to the V/USY catalyst reduced the gasoline S content by additional 12.3%, i.e., 237% improvement over the V/USY reference catalyst.

Example 7

Fluid Catalytic Cracking Evaluation of Series 2 Catalysts after Cyclic Steaming

The performances of the V and Ce+V catalysts from Example 2 after cyclic steam deactivation are summarized in this example. The catalysts of Example 2 were deactivated by cyclic steaming as described above (ending-oxidation) and were then blended with an equilibrium catalyst from an FCC unit in 25:75 weight ratio. The equilibrium catalyst has very low metals level (120 ppm V and 60 ppm Ni). The evaluation results obtained with the VGO feed are summarized in Table 8.

29

Tabl 8
Catalytic Cracking Performance of V vs. Ce+V/USY/ Silica-Sol Catalyst

	ECat Base Case	+ 25% V/USY cat (Cat C)	+ 25% Ce+V/USY (Cat D)	+ 25% Ce+V/USY (Cat E)
MAT Product Yields				
Conversion, wt%	70	70	70	70
Cat/Oil	2.8	3.7	3.6	3.4
H2 yield, wt%	0.03	+0.12	+0.13	+0.12
C1 + C2 Gas, wt%	1.5	+0.2	+0.2	+0.1
Total C3 Gas, wt%	5.5	+0.1	+0	-0.1
C3= yield, wt%	4.7	+0	+0	-0.1
Total C4 Gas, wt%	11.1	+0	+0	-0.2
C4= yield, wt%	5.8	+0.1	+0.1	+0
iC4 yield, wt%	4.6	-0.1	-0.2	-0.2
C5+ Gasoline, wt%	49.4	-1.0	-0.9	-0.5
LFO, wt%	25.6	-0.1	+0	+0.2
HFO, wt%	4.4	+0.1	+0	-0.2
Coke, wt%	2.3	+0.6	+0.5	+0.5
Cut Gasoline S, PPM	579	283	243	224
% Reduction in Cut Gasoline S	Base	51.1	58.1	61.3

Table 8 compares the FCC performances of V/USY and Ce+V/USY/ Silica-Sol additive catalysts after cyclic steam deactivation (ending-oxidation). Compared to the ECat base case, addition of V/USY and Ce+V/USY catalyst made slight changes in the overall product yield structure. There were moderate increases in hydrogen and coke yields. Also a small changes in C4- gas yield gasoline, light cycle oil and heavy fuel oil were observed. Addition of the V/USY and Ce+V/USY catalysts changed the gasoline S concentration substantially. When 25 wt% of Catalyst C (V/USY - reference catalyst) was blended with an equilibrium FCC catalyst, 51.1 % reduction in gasoline sulfur concentration was achieved. In comparison, the Ce+V/USY catalysts (Catalysts D and E) gave 58.1% and 61.3% reduction in gasoline S, respectively. Addition of Ce to the V/USY catalyst reduced the gasoline S content by additional 7.0 – 10.2%, i.e., up to 20% improvement over the V/USY reference catalyst.

The product yields data of the V/USY and Ce+V/USY catalysts indicate that the yield changes from the ECat is due to addition of vanadium to the USY catalyst. The product yields of V/USY catalyst is comparable to those of Ce+V/USY catalysts except the gasoline S level. These results suggest that Ce increases the gasoline sulfur reduction activity of the V/USY additive catalyst with little effect on product yields.

Example 8

Fluid Catalytic Cracking Evaluation of Series 3 Catalysts, Study of Promotional Effects

Performances of the Ce and Ce+V catalysts from Example 3 after cyclic steaming deactivation (ending-reduction) as described above, are summarized in this example. The deactivated catalysts were blended with an equilibrium catalyst from an FCC unit in 25:75 weight ratio. The equilibrium catalyst has very low metals level (120 ppm V and 60 ppm Ni). The results obtained with the VGO feed are summarized in Table 9.

31

Table 9

Catalytic Cracking Performance of Ce vs. Ce+V/USY/ Silica-Clay Catalysts

	ECat Base Case	+ 25% Ce/USY (Cat G)	+ 25% Ce+V/USY (Cat H)	+ 25% Ce+V/USY (Cat I)
MAT Product Yields				
Conversion, wt%	70	70	70	70
Cat/Oil	3.2	3.4	3.7	3.9
H2 yield, wt%	0.04	+0	+0.07	+0.07
C1 + C2 Gas, wt%	1.5	+0.1	+0.1	+0.1
Total C3 Gas, wt%	5.7	+0.1	-0.1	+0
C3= yield, wt%	4.8	+0	+0	+0
Total C4 Gas, wt%	11.5	+0	-0.3	-0.1
C4= yield, wt%	5.7	+0	+0.1	+0.1
iC4 yield, wt%	4.9	+0	-0.3	-0.2
C5+ Gasoline, wt%	48.8	-0.2	-0.2	-0.7
LFO, wt%	25.5	+0	+0.1	+0.1
HFO, wt%	4.5	+0	-0.1	-0.1
Coke, wt%	2.4	+0	+0.3	+0.6
Cut Gasoline S, PPM	486	487	341	351
% Reduction in Cut Gasoline S	Base	0	29.8	27.7

5

Table 9 compares FCC performances of Ce/USY and Ce+V/USY/ Silica-clay additive catalysts after cyclic steam deactivation (ending-reduction). Compared to the ECat base case, addition of the Ce/USY catalyst made almost no changes in overall product yields. Addition of the Ce+V/USY catalyst made slight changes in the overall product

10   yield structure. There were moderate increases in hydrogen and coke yields, as well as slight changes in C4- gas, gasoline, light cycle oil and heavy fuel oil yields. Addition of the Ce/USY catalysts made a no change in the gasoline S concentration. In contrast, Ce+V/USY catalysts (Catalysts H and I, invention) gave 29.8% and 27.7% reduction in gasoline S, respectively. These results indicate that cerium by itself does not have any

15   gasoline sulfur reduction activity. Cerium appears to have a promotional effect for vanadium to increase the activity of a V/USY gasoline sulfur reduction additive catalyst.

Example 10

Fluid Catalytic Cracking Evaluation of Ce+V/ USY/ Silica-Sol Catalysts

5   The Ce+V USY catalyst from Example 4 was evaluated in a circulating fluidized cracking unit for 40 days in combination with a typical FCC catalyst using the severely hydrotreated FCC feed of Table 5 (CFHT Feed). The base FCC equilibrium catalyst has very low metals level (200 ppm V and 130 ppm Ni). For the first 15 days, a 50/50 blend of fresh FCC catalyst and the Ce+V USY catalyst from Example 4 was added to the FCC

10 regenerator at about 1.4% of the catalyst inventory pre day. From 15th to 40th day, a 85/15 blend of the fresh FCC catalyst and the Ce+V USY catalyst was added to the FCC regenerator at about 1.4% of the catalyst inventory per day. The regenerator temperature was maintained at approximately 705°C (1300°F) throughout the evaluation. Two equilibrium catalyst (ECat) samples were collected: the first was sampled before the

15 Ce+V/USY addition (base case) and the second at 40th day. Based on Ce and V analysis, the loading of the Ce+V USY catalyst is estimated as 12%.

The ECat samples were evaluated in a circulating riser pilot unit using the CFHT feed in Table 4. To determine the sulfur content of the distillate fractions boiling above the

20 gasoline range, the syncrude was distilled via atmospheric distillation to separate the gasoline. Then the bottom fraction was further vacuum distilled to generate two fractions of LCO (light LCO and heavy LCO) and HFO. The ranges of cut points for distillations are C5+ to 220°C (C5+ -430°F) for gasoline, 220° – 310°C (430° - 590°F) for light LCO, 310° – 370°C (590° - 700°F) for heavy LCO, and 370°C+ (700°F+) for HFO. The sulfur

25 species in a LCO sample were quantitated using a GC equipped with J&W 100 m DB-Petro column and Sievers 355B sulfur detector. An example of LCO sulfur GC is shown in Figure 1 with sulfur GC speciation. The concentration of each LCO sulfur species was calculated based on the percentage of the sulfur species from the GC and the total sulfur content measured by XPS method.

30

FCC performances of the catalysts are summarized in Table 10, where the product selectivity was interpolated to a constant conversion, 70wt% conversion of feed to 220°C- (430°F-) material.

Table 10
Catalytic Cracking Performance of Ce+V/USY/ Silica-Sol Catalyst

	ECat Base Case	+ 12% Ce+V/USY (Cat J)
Riser Product Yields		
Conversion, wt%	70	70
Cat/Oil	6.5	6.4
		Incremental Yield
H_2 yield, wt%	0.02	+0.0
Total C_3, wt%	4.8	+0.0
Total C_4, wt%	9.3	+0.1
C_5^+ Gasoline, wt%	51.9	-0.2
LFO, wt%	24.0	-0.2
HFO, wt%	6.1	+0.1
Coke, wt%	2.6	+0.1
Cut Gasoline S, ppm	100	79
Light LCO Sulfur, ppm	815	599
Heavy LCO Sulfur, ppm	1957	1687
HFO Sulfur, ppm	2700	1700
% Reduction in Gasoline Sulfur	Base	21
% Reduction in Light LCO S	Base	27
% Reduction in Heavy LCO S	Base	14
% Reduction in HFO Sulfur	Base	37
Wt% S of spent catalyst	<0.06	<0.06

Compared to the ECat base case, addition of the Ce+V/USY catalyst made small changes in the overall product yield structure. There were negligible increases in H_2 and coke yields. Also little changes in C_4^- gas, gasoline, light cycle oil and heavy fuel oil yields were observed. Addition of the Ce+V/USY catalyst changed the gasoline S concentration substantially. When 12 wt% of Ce+V/USY catalyst was blended in the equilibrium FCC catalyst, 21 % reduction in gasoline sulfur concentration was achieved. In addition to the gasoline sulfur reduction, substantial sulfur reductions in LCO and HFO were observed.

The sulfur species in the light LCO fraction were analyzed using a sulfur GC. The concentration of each organo-sulfur class was as shown in Table 11 and Figure 2 for light LCO.

Table 11
Sulfur Speciation of Light LCO from CFHT Feed

	ECat Base Case	+12% Ce+V/USY (Cat J)
C_3^+Thiopenes	4	1
Benzothiophene	20	14
C_1-Benzothiophenes	141	106
C_2-Benzothiophenes	237	174
C_3^+-Benzothiophenes	295	215
Dibenzothiopehene	17	14
C_1-Dibenzothiophenes	47	34
C_2-Dibenzothiophenes	32	25
C_3-Dibenzothiophenes	20	13
C_4^+-Dibenzothiophenes	3	1

As shown in Figure 2, the light LCO contains mainly benzothiophene sulfur species. The sulfur reductions were more prominent for substituted benzothiophenes such as C_1- through C_3^+-benzothiophenes. The results are quite unexpected since substituted benzothiophenes are bulkier, and they are expected to be harder to crack and desulfurize in FCC.

The sulfur species in the heavy LCO fraction were as shown in Table 12 and Figure 3. The heavy LCO contains mainly dibenzothiophene sulfur species. The sulfur reductions were more prominent for substituted dibenzothiophenes such as C_1- through C_4^+-dibenzothiophenes. The results are quite unexpected since substituted dibenzothiophenes are bulkier and expected to be harder to crack and desulfurize in FCC.

Table 12
Sulfur Speciation of Heavy LCO from CFHT Feed

	ECat Base Case	+ 12% Ce+V/USY (Cat J)
Benzothiophene	0	0
C_1-Benzothiophenes	2	1
C_2-Benzothiophenes	12	7
C_3^+-Benzothiophenes	128	86
Dibenzothiopehene	65	54
C_1-Dibenzothiophenes	361	312
C_2-Dibenzothiophenes	537	480
C_3-Dibenzothiophenes	475	425
C_4^+-Dibenzothiophenes	378	322

5

The sulfur reduction catalyst is active in reducing benzothiophene and dibenzothiophene sulfur species as well as thiophene sulfur species. The reduction of sulfur takes place predominantly for substituted benzothiophenes and substituted dibenzothiophenes. These results suggest that C-S bonds in alkyl substituted-thiophenes are more reactive
10 and susceptible to cracking.

The facile sulfur reduction of substituted-thiophenes, substituted-benzothiophenes, and substituted-dibenzothiophenes was quite unexpected and will enhance the effectiveness of a subsequent LCO hydrodesulfurization process. It is well known for LCO
15 hydrodesulfurization process that methyl and/or alkyl substitution of benzothiophene and dibenzothiophene makes desulfurization reactivity of the organic sulfurs decline substantially and become "hard sulfur" or "refractory sulfur". Our LCO containing a lower amount of substituted benzo and dibenzothiophenes will generate a diesel fuel with a lower sulfur content after a hydrodesulfurization process than the comparable LCO
20 generated by a conventional FCC catalyst.